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THE RESISTANCE OF BERYLLIUMIZED SURFACES
TO HIGH TEMPERATURE SLAG CORROSION

Research and Development Report 910088
NS-013-120

22 October 1958

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By

W. J. Greenert

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U. S. NAVAL ENGINEERING EXPERIMENT STATION

Annapolis, Maryland

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W. J. Greenert
W. J. Greenert

Mechanical Metallurgy Branch

Approved by

W. L. Williams

W. L. Williams
Head
Metals Division

Forwarded by

R. L. Mohan
R. L. Mohan
Captain, USN
Commanding Officer
and Director

ABSTRACT

Beryllium diffused surfaces on Type 310 stainless steel, Inconel, and Haynes Stellite 31 were evaluated for resistance to fuel-oil-ash slags at elevated temperature. Considerable improvement in resistance to corrosion caused by vanadium bearing slags was induced in the stainless steel. However, a decreased resistance to sulfate-chloride corrosion was shown by all surfaces, while the over-all resistance of the Haynes Stellite was significantly reduced by the berylliumizing process. A metallographic examination of the coatings is presented.

E.E.S. REPORT 910088

ADMINISTRATIVE INFORMATION

This investigation was authorized by Bureau of Ships letter
A11/NS-013-120 (343) serial 343-168 of 21 April 1958.

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REPORT OF INVESTIGATION

INTRODUCTION

The performance of fuel-burning equipment is limited by the rapid corrosion of refractory and ordinary heat resisting surfaces by vanadium bearing fuel-oil-ash, references (a) and (b). Severe attack on heat resisting steels and alloys also occurs from alkali-earth sulfates mixed with chloride, reference (c). The presence of these substances is reasonably assured in the combustion of fuel in marine equipment. One approach to this limiting problem is to reduce or prevent the corrosion of otherwise suitable materials by the application of protective coatings or surfaces. Aluminum coatings on stainless steel were shown in references (d) and (e) to be no solution to the fuel-oil-ash problem. Various refractory coatings, reference (f), likewise have failed to provide the necessary resistance.

A process whereby beryllium is deposited and diffused into metallic surfaces has been developed by The Metallic Surfaces Research Laboratories, Limited, Oxbridge, Middlesex, Great Britain. The purpose of the process is to provide a surface resistant to vanadium pentoxide corrosion at elevated temperatures. The process apparently is a highly protected proprietary item; thus, little specific information has yet been obtained.

The Bureau of Ships, by negotiation through the Naval Attache and Naval Attache for Air, Navy 100, Fleet Post Office, New York, New York, arranged to have specimens treated by this process. Such arrangements were requested in reference (g). The processed specimens were evaluated at the Station for resistance to fuel-oil-ash corrosion. The results of this evaluation are presented herein.

MATERIALS

Four specimens each of stainless steel, Inconel, and Haynes 188 were "berylliumized." The size of each specimen was 1/4" by 1/8" by 2-1/2". Specific characteristics of the materials from which the specimens were fabricated are presented in Table 1.

Table 1

Base Materials Subjected to Berylliumizing

Material	Condition	Composition, wt %
Type 310 stainless steel	1/4" rolled plate, annealed	51.83 Fe, 25.30 Cr, 20.32 Ni, 0.66 Si, 1.65 Mn, 0.05 C, 0.16 Cu
Inconel	3/4" ϕ hot rolled	6.00 Fe, 13.05 Cr, 76.03 Ni, 0.42 Si, 0.33 Co, 0.70 Ti, 1.30 Al
Haynes Stellite 31	1/4" plate, aged	1.37 Fe, 24.71 Cr, 9.76 Ni, 7.62 W, 0.49 Si, 0.56 Mn, 0.5C, Balance Co

METHOD OF TEST

A cursory examination of the effect of processing on the materials was made by weight change analysis and visual and metallographic inspections.

The berylliumized specimens were subjected to high temperature oxidation and corrosion by three oxidation-accelerating slags. These slags were:

1. A sulfated vanadium slag formed from 70% V_2O_5 + 30% Na_2SO_4 . This slag induced on Type 310 stainless steel a corrosion rate similar to that found on failed superheater tube support plates removed from service boilers.

2. A nonsulfated, vanadium slag formed from 79% V_2O_5 + 21% $NaVO_3$. This slag induced the highest oxidation rate observed to date for vanadium slags. The constituent proportion of this slag was equivalent to a 6:1 ratio of V_2O_5/NaO .

3. A nonvanadium slag formed from 90% Na_2SO_4 + 10% $NaCl$. This slag was termed the sulfate-chloride slag. The constituents used in these slags were chemically pure (CP) grade reagents.

In the vanadium slag corrosion tests, the specimens were precontaminated by immersing in the specific slag for two hours at 1600°F. In this manner, a contaminated surface was prepared which was then tested in the oxygen consumption apparatus. A description of the apparatus and test procedure is contained in reference (a). In test, the specimens were maintained at 1600°F in an oxygen environment at one atmosphere pressure. The consumption of oxygen by the surface was periodically measured. Duration of the tests was approximately 23 hours. The weight of material corroded during test was also determined. The specimens were descaled after test by the molten-sodium hydride-quench procedure.

Tests in the sulfate-chloride slag differed from the above procedure in that there was no precontaminating step. Instead, the specimen, with five grams of slag mix, was contained in a ceramic boat in the oxygen consumption apparatus during test.

RESULTS OF TESTS

The berylliumizing process induced average weight gains in the various materials as shown in Table 2.

Table 2

Weight Change in Berylliumizing

Material	Weight Gain gm/sq in.	Standard Deviation, n = 4
Type 310 stainless steel	0.0232	0.00065
Inconel	0.0275	0.00293
Haynes Stellite 31	0.0184	0.00077

The surfaces of the specimens, which were of a fine machine finish prior to berylliumizing, had a mottled white and gray color and approximately 80 microinches rms surface roughness after berylliumizing. A fine white powder was obviously expelled on handling the specimens.

Photomicrographs of the processed surfaces are shown in Figure 1. Total depth of the coating or diffused layer appeared to be 0.0044" for the stainless steel, 0.0016" for the Inconel, and 0.0016"

for the Stellite. Diffusion to greater depth probably occurred, but the concentration was not sufficient for phase formation, and the maximum depth could not be indicated by the etching technique. Extensive diffusion occurred in the berylliumized layer on the Type 310 stainless steel. Complex metallic phases were distributed from the surface to the base metal interface. The variable etching rates, which occurred in selected reagents, indicated the surface phases to be high in beryllium. Some needles of a high beryllium phase, however, extended to the substrate interface. Signs of eutectic phases were also found in the berylliumized layer. Phase diagrams, reference (h), show that nickel and iron series of alloys with beryllium contain complex intermetallic compounds with associated eutectic compositions. The locations of nonmetallic inclusions in the diffusion layers indicated that the diffusion or growth of the layers was predominately inward into the base material. Both the Inconel and Stellite also showed characteristics of extensive diffusion, although somewhat different than the Type 310 stainless steel. Diffusion of beryllium in the base material beyond the phase concentration line was quite obvious in the Inconel. Grain boundary diffusion was apparent in this low concentration area. Little or no diffusion in the substrate was indicated in the Type 310 steel or the Stellite.

Results from the oxidation-corrosion tests of the berylliumized surfaces are shown in Table 3 and the graphs of Figures 2, 3, and 4. Included in the graphs are nonberylliumized surfaces for comparison. Figure 5 are photographs of berylliumized surfaces after test.

Table 3
Oxidation of Berylliumized Surfaces

Mat. No.	Surface Con. aminant	MI of O_2 /in. ²				Total Weight Loss of Specimen, gm	Remarks
		1 Hr	2 Hr	3 Hr	Extended Time		
Type 310 stainless steel	No slag	3	4	4	10 at 23 hr		No obvious damage or corrosion
	70% V_2O_5 + 30% Na_2SO_4	1.5	5.7	6	20 at 23 hr	0.2237	Slight surface erosion
	70% V_2O_5 + 21% $NaVO_3$	18	21	24	55 at 23 hr	0.9219	Local large pit corrosion, definite depth limit
	90% Na_2SO_4 + 10% $NaCl$	418	488	508	564 at 23 hr	5.2044	Massive cratering and erosion
Inconel 61	No slag	1	1	1	1 at 23 hr		No obvious damage or corrosion
	70% V_2O_5 + 30% Na_2SO_4	32	68	105	495 at 23 hr	5.1790	Massive cratering, selective corrosion (spongy)
	70% V_2O_5 + 21% $NaVO_3$	19	27	35	94 at 23 hr	3.3678	General surface erosion, pebbly surface
	90% Na_2SO_4 + 10% $NaCl$	35	48	66	248 at 22 hr	3.8902	General microscopic pit erosion
Stellite	No slag	4	4	4	4 at 23 hr		No obvious damage or corrosion
	70% V_2O_5 + 30% Na_2SO_4	23	38	49	112 at 23 hr	2.0007	Small cratering in general erosion
	70% V_2O_5 + 21% $NaVO_3$	45	51	53	79 at 21 hr	2.3818	Massive cratering, extensive on edges
	90% Na_2SO_4 + 10% $NaCl$	71	514	649	940 at 24 hr	15.6693	Massive erosion, complete deterioration

The berylliumized Type 310 stainless steel surfaces exhibited considerable resistance to vanadium slags over a 23-hour history. No metallic surfaces studied to date have shown greater resistance. However, the berylliumized stainless steel showed poor resistance to the sulfate-chloride slag. In fact, the processed surface was less resistant than the base material.

The berylliumized Inconel was highly resistant to vanadium slags. However, no improvement was considered to have been induced by the process, as Inconel itself is highly resistant to vanadium slags. As with the stainless steel, the berylliumized Inconel showed less resistance to sulfate-chloride slag than an unprocessed Inconel surface.

The berylliumized Haynes Stellite 31 surfaces were less resistant to all slags than the unprocessed surfaces. The berylliumized surfaces suffered exceptionally severe damage from the sulfated-vanadium slag. The resistance to this slag of the processed surface was estimated to be 30% of the uncoated Haynes Stellite 31 material.

The weight losses of specimens during test supplemented the oxygen consumption indications of corrosion. Likewise, the appearance of the surfaces after test, shown in Figure 5, indicated similar degrees of corrosion. It is apparent from the photographs that different corrosion mechanisms operated on the different surfaces. The sulfated-vanadium slag, somewhat noncorrosive to berylliumized Type 310 steel, was microscopically selective and severe on the Stellite, while being grossly selective or cratering and moderately corrosive to the Inconel. The nonsulfated vanadium slag caused a sparse, pit type attack on the berylliumized Type 310 steel surface, a general erosion on the Haynes Stellite 31, and a massive cratering type attack on the Inconel. The sulfate-chloride slag resulted in a catastrophically severe corrosion to all berylliumized surfaces and yet showed evidence of different mechanisms for each. A massive cratering attack occurred on the Type 310 stainless steel, a microscopic, pit type erosion occurred on the Haynes Stellite 31, and complete destruction via erosion and wastage occurred on the Inconel.

CONCLUSIONS

The following conclusions are derived from the foregoing results:

1. The berylliumizing process produces a diffused alloy surface of microscopic depth on Type 310 stainless steel, Inconel, and Haynes Stellite 31.

2. The berylliumized Type 310 stainless steel and Inconel surfaces are highly resistant to vanadium bearing laboratory slags. Such surfaces, however, are less resistant to sulfate-chloride slag than the untreated base materials.

3. A berylliumized Haynes Stellite 31 surface is less resistant to simulated fuel-oil-ash slags than untreated Haynes Stellite 31.

DISCUSSION

The effectiveness of berylliumizing for increasing resistance to vanadium bearing fuel-oil-ash is a function of the base material. Of the three materials investigated, only the iron base, Type 310 stainless steel was amenable to improvement, while the natural high resistance of Haynes Stellite was substantially reduced. It is anticipated that, at present, the resistance of various treated alloys must be determined individually. However, since alloys of a particular system are expected to behave somewhat similarly, it is considered that the iron base alloys are the most appropriate for a subsequent study. A program for evaluating various berylliumized, ferrous alloy surfaces will be discussed with the Bureau of Ships.

The lack of improved resistance to sulfate-chloride slag shown by the berylliumized surfaces somewhat vitiates the use of such surfaces in marine firesides. Until the complex phases of marine fireside corrosion are better understood and the primacy of either vanadium or sulfate-chloride corrosion established, the true worth of berylliumized surfaces for naval use cannot be determined from laboratory study. It is anticipated that future evaluations of berylliumized surfaces will contain the elements of a service exposure. This can be provided by the insertion of suitable specimens in selected locations in ships' firesides. Nevertheless, initial evidence for a selection for service exposure must come from the simple, expedient, laboratory type tests.

Considerable difficulty was experienced in maintaining correspondence regarding the processing of specimens. As a result, little information of the process is available. The Chromizing Company, 1721 East 47th Street, Los Angeles 58, California, is an associate of The Metallic Surfaces Research Laboratories, Limited. The Chromizing Company has recently been named as a domestic exhibitor of the berylliumizing process. Their co-operation in future investigations of this process should enable a more rapid processing of specimens and provide better basic information of the berylliumizing treatment.

Beryllium and many of its compounds are extremely toxic. The beryllium ion is considered to be one of the most toxic of any industrial material. Physical manifestations of beryllium induced diseases are chemical pneumonitis, berylliosis, and skin reactions, such as dermatitis, ulcers, and tumors. The contamination limit, as established by the U. S. Atomic Energy Commission, is two micrograms per cubic meter as an average concentration for in-plant atmospheres; reference (i). It is, therefore, apparent that extreme precautions are essential in working with beryllium or its compounds. A program involving any but the most cursory manipulations will require substantial, specialized equipment.

REFERENCES

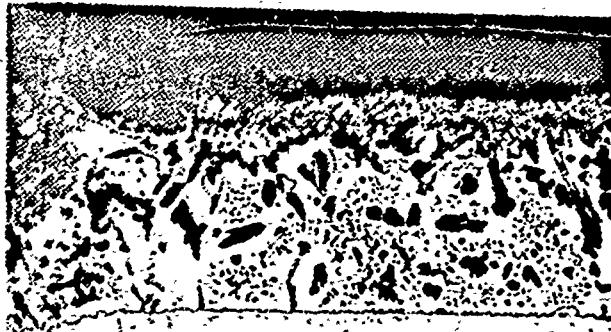
- (a) EES Rept 040007BH of 17 Nov 1955
- (b) Frederick, S. H., and Eden, T. F., "Corrosion Aspects of the Vanadium Problems in Gas Turbines," Proc of Inst of Mechanical Engineers, vol. 168, No. 3, 1954
- (c) Shirley, H. T., "Effects of Sulfate-Chloride Mixtures in Fuel-Ash Corrosion of Steels and High-Nickel Alloys," Jul Iron and Steel Institute, Feb 1956, pp. 144-153
- (d) Srawley, J. E., "Aluminum Coatings on Stainless Steel," NRL Rept 4838, 17 Oct 1956
- (e) EES Rept 040007CW of 8 Feb 1957
- (f) Lewis, A., and Graham, R., "The Effect of Fuel-Oil-Ash on Surface Coatings," Thorton Research Center Rept M, 149, Jul 1954
- (g) BUSHIPS ltr J1 (343) ser 343-77 of 27 Feb 1957
- (h) White, D. W., Jr., and Burke, J. E., The Metal Beryllium, American Society for Metals, Cleveland, Ohio, 1955, pp. 562-563
- (i) Ibid, p. 627

RECOMMENDATIONS

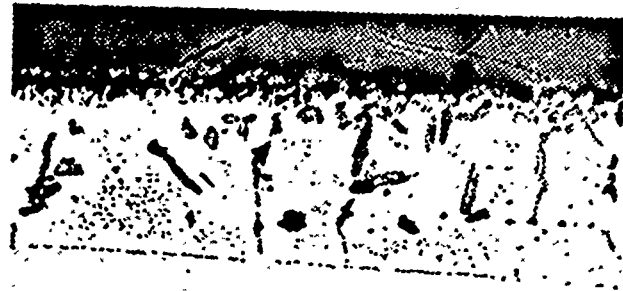
The low corrosion resistance of certain berylliumized surfaces requires that, at present, berylliumized surfaces not be advocated for general use in the naval service. However, it is recommended that further investigation of such surfaces be conducted. The increased resistance shown by the Type 310 stainless steel may be indicative of an improvement exclusive to certain alloys. At this phase of the study, it is suggested that berylliumized surfaces on iron and iron-chromium base alloys be investigated.

Type 310 Stainless Steel

Glyceresia Etch

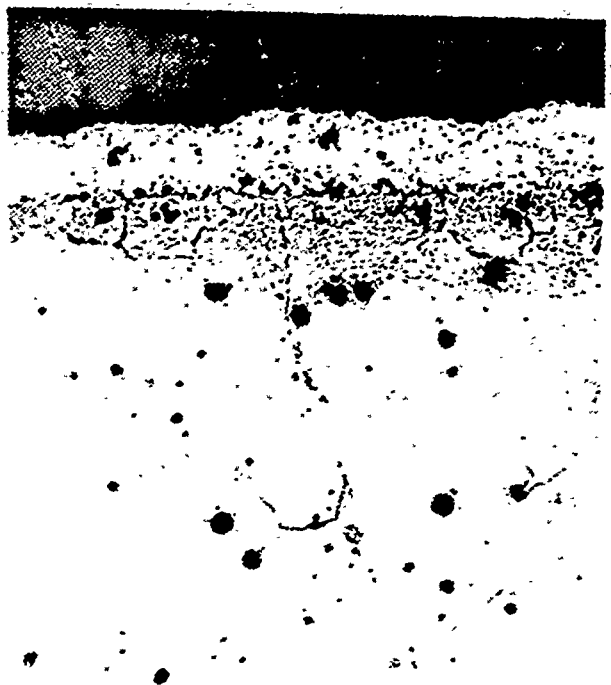


Ferric Chloride Etch



Inconel

Ferric Chloride Etch



Haynes Stellite 31

Murakami Etch

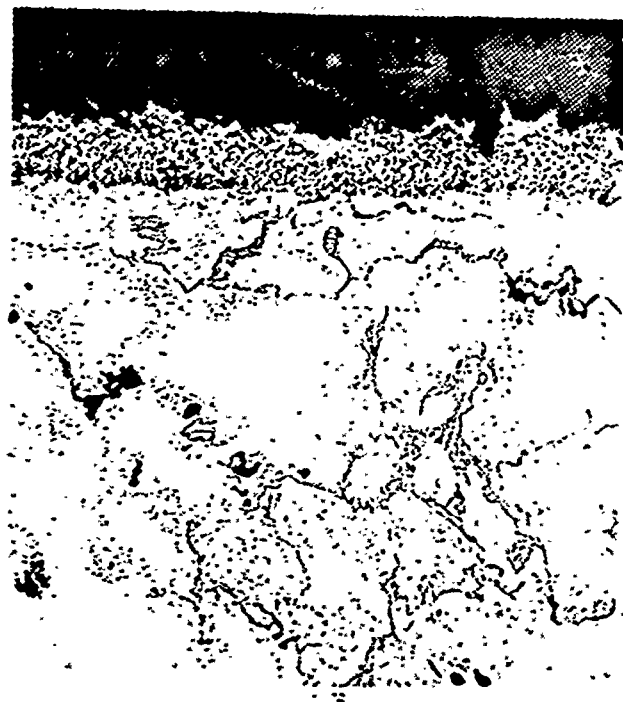


Figure 1
Photomicrographs of Beryllium Diffused Metal Surfaces (X250)

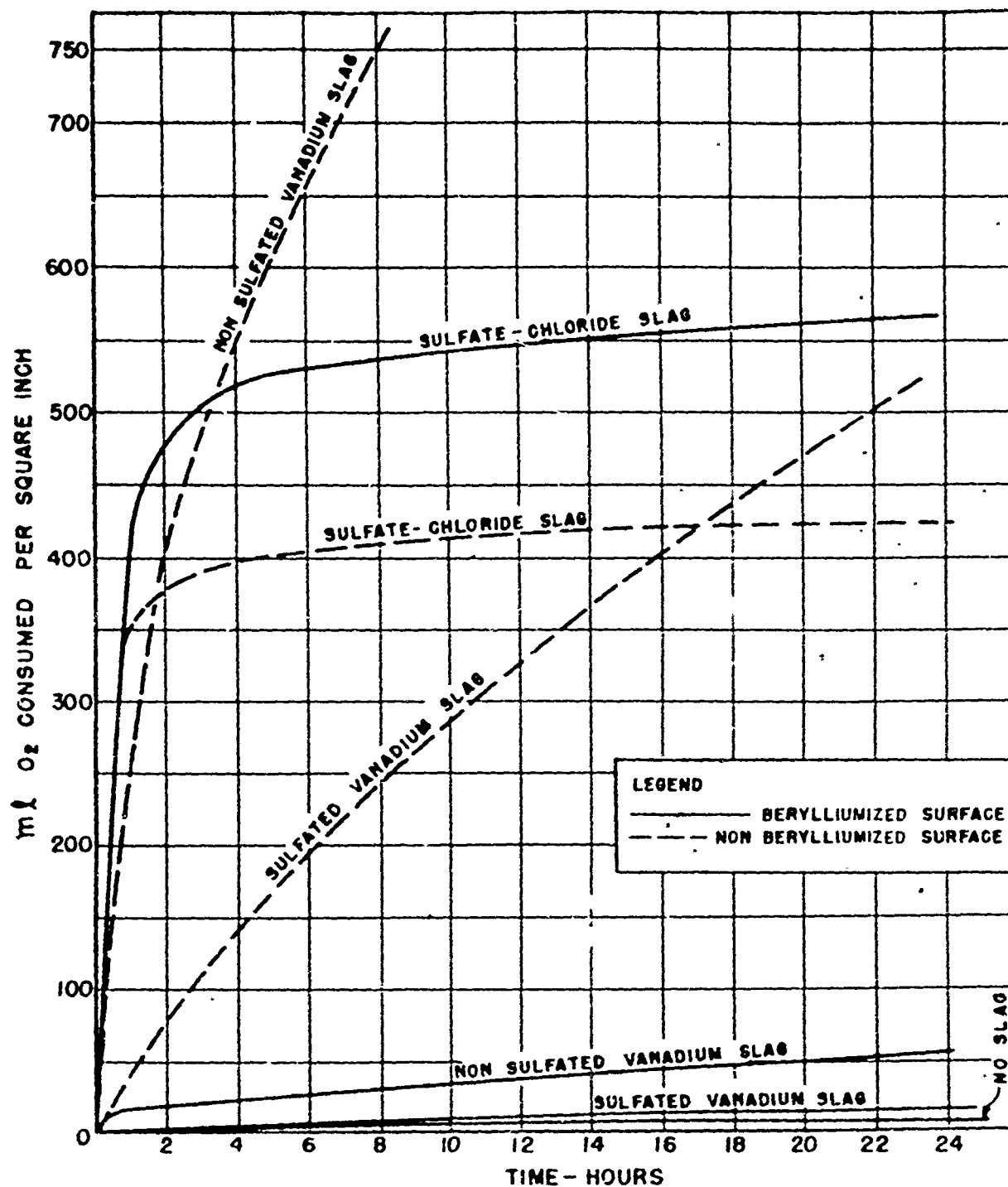


Figure 2
Oxidation of Berylliumized Type 310 Stainless Steel

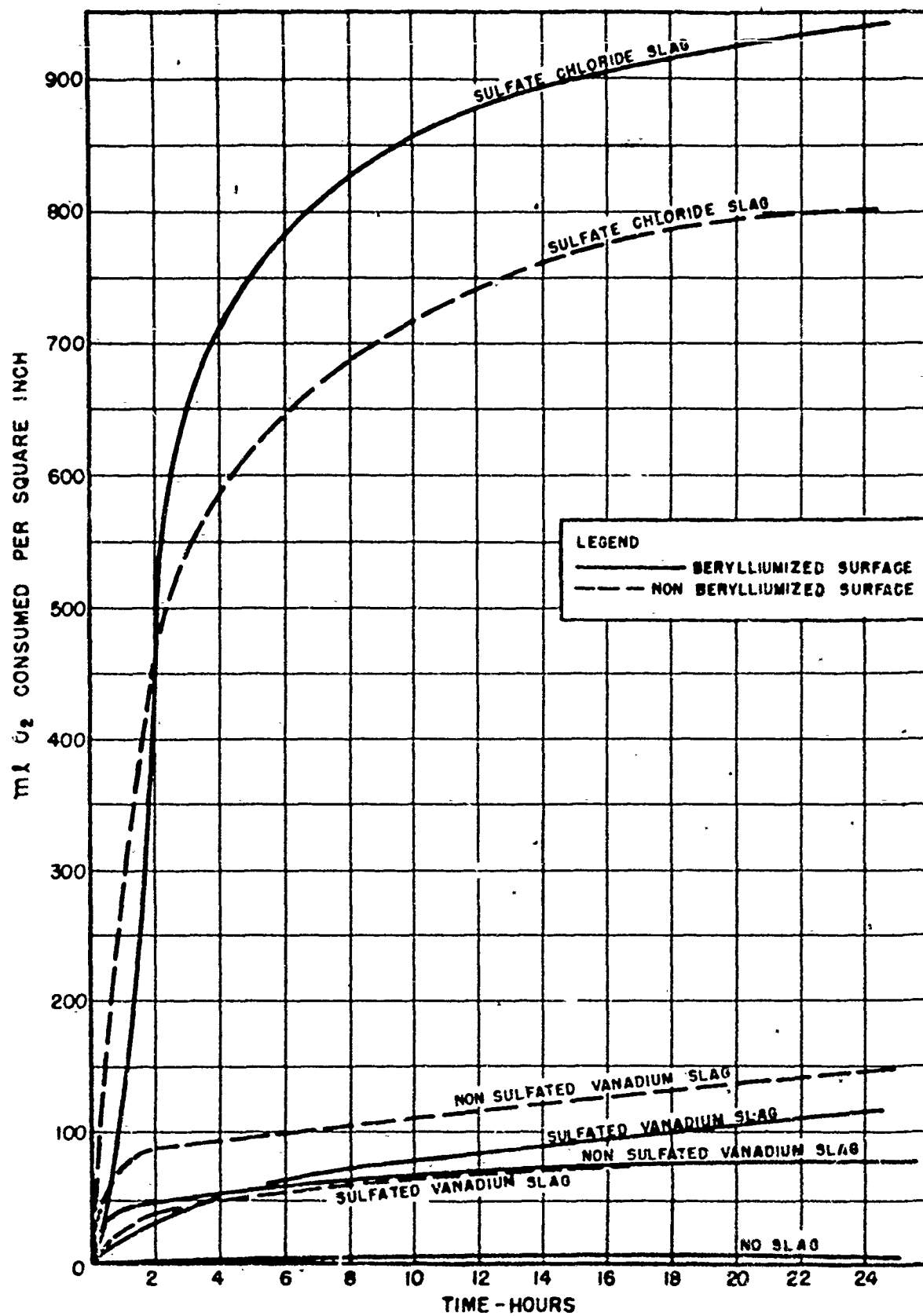


Figure 3
Oxidation of Berylliumized Inconel

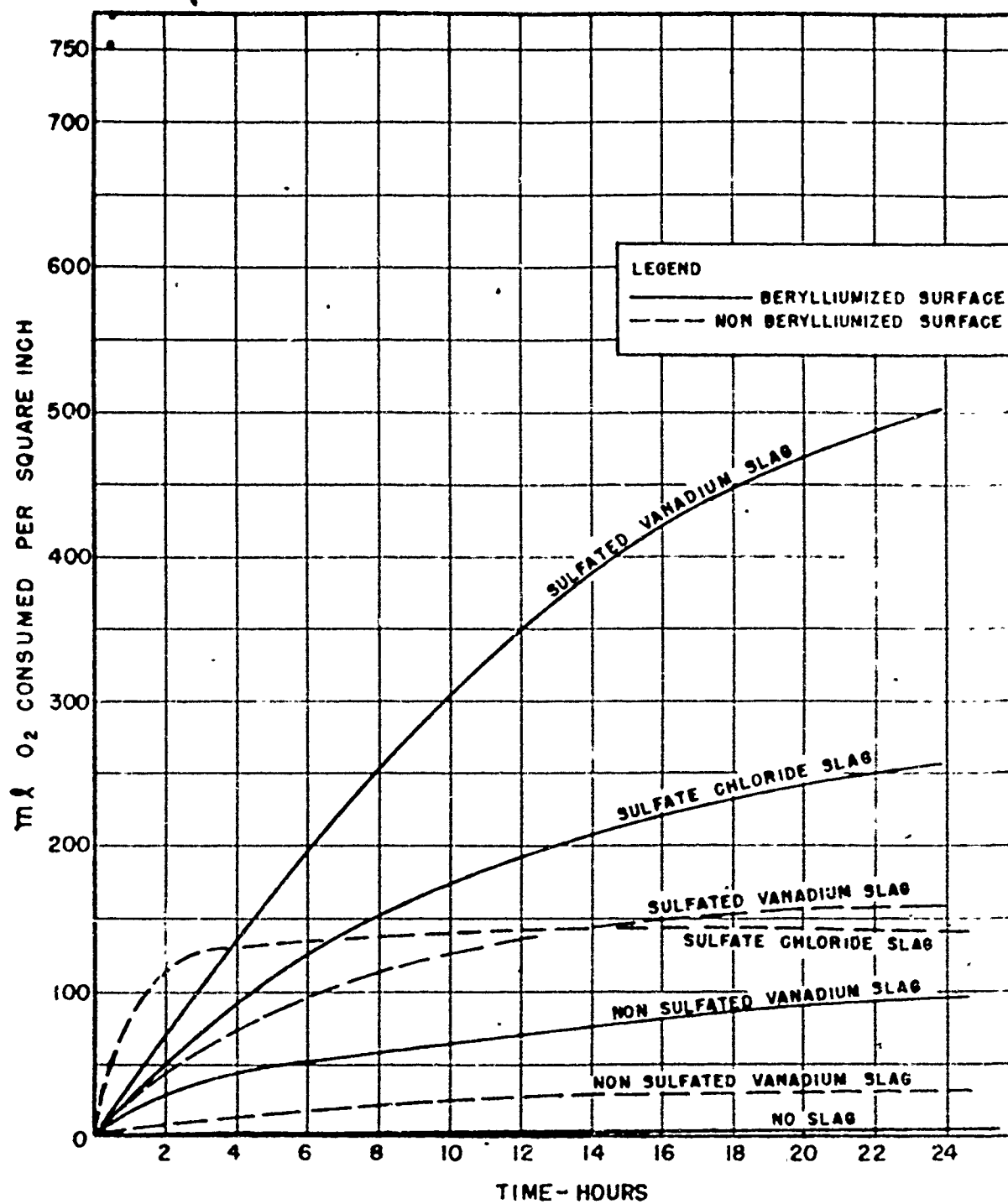


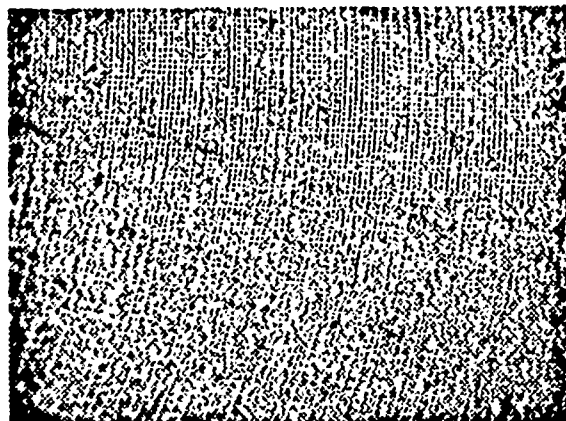
Figure 4
Oxidation of Berylliumized Haynes Stellite 31

Base Material:

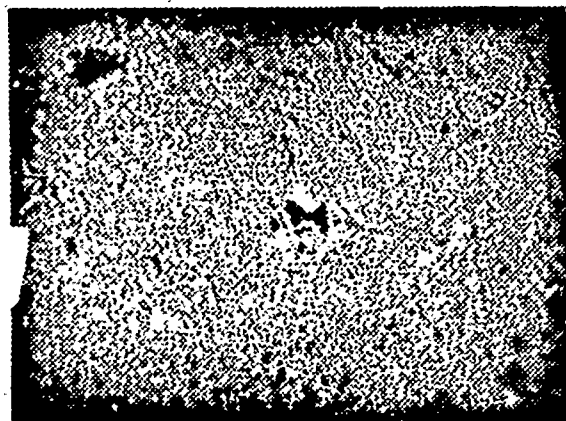
Type 310 Stainless Steel

Corrodent

Sulfated Vanadium Slag
70% V_2O_5 + 30% Na_2SO_4



Nonsulfated Vanadium Slag
79% V_2O_5 + 21% $NaVO_3$



Sulfate-Chloride Slag
90% Na_2SO_4 + 10% $NaCl$

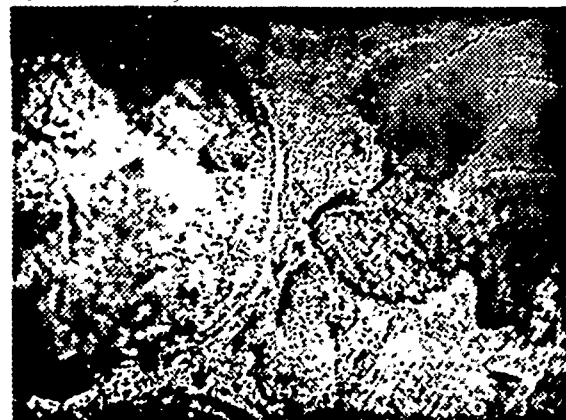


Figure 5
Photomicrographs of Berylliumized Surfaces Corroded by
Simulated Fuel-Oil-Ash (X15)

Inconel

Haynes Stellite 31

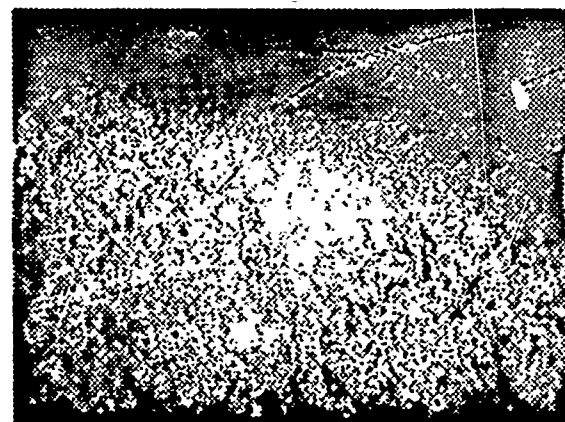
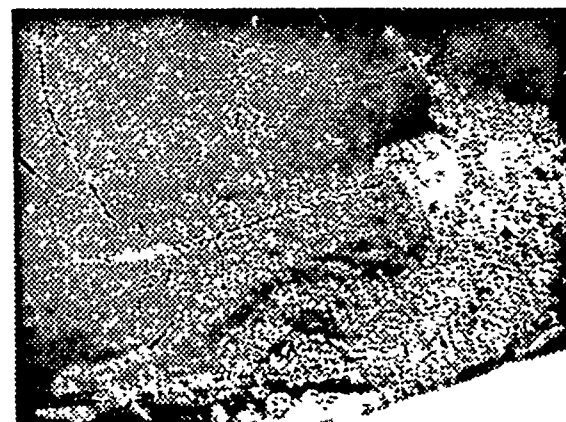
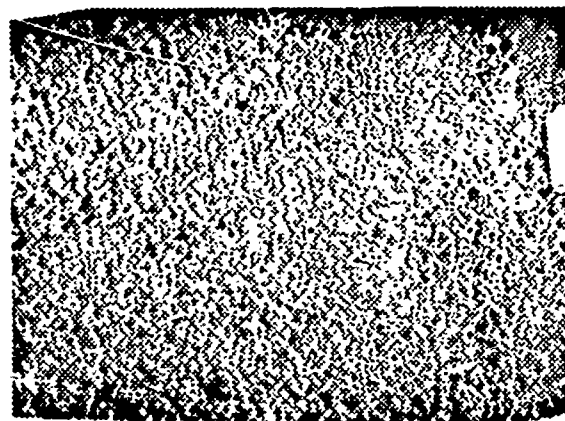
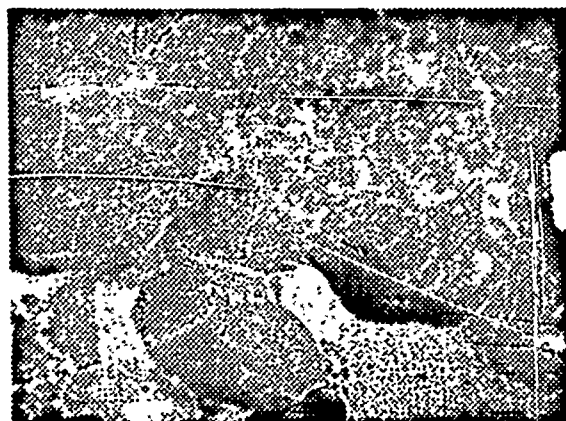
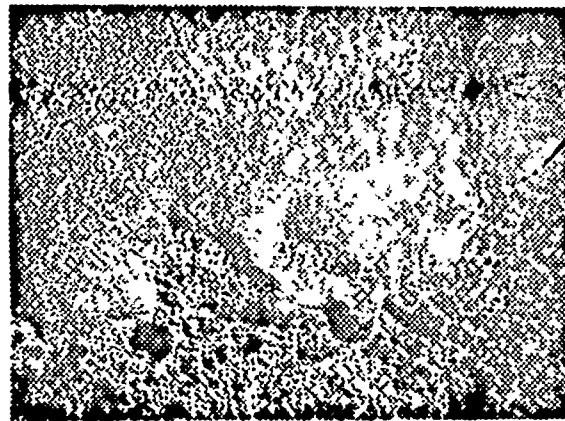
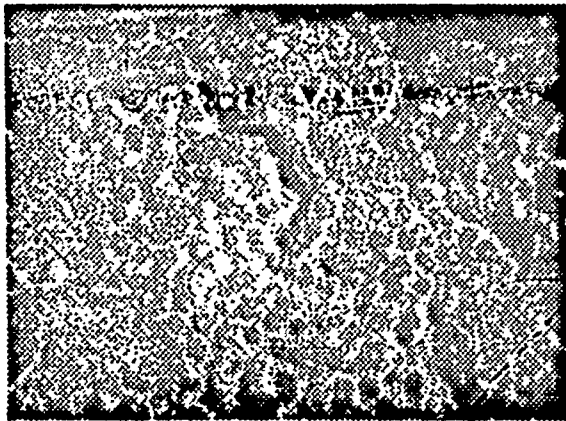


Figure 5 (Cont)
Photomicrographs of Berylliumized Surfaces Corroded by
Simulated Fuel-Oil-Ash (X15)